

# Electronic Properties of TiO<sub>2</sub> Nanotubes

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New quasi-one-dimensional (1D) titania nanostructures - single-walled nanotubes formed by rolling [101] planes of TiO<sub>2</sub> (anatase phase) are modeled and their electronic properties and bond orders indices are studied using the tight-binding band theory. We show that all zigzag ( $n,0$ )- and armchair ( $n,n$ )-like nanotubes are uniformly semiconducting, and the band gap tends to vanish as the tube diameters decrease. It was established that the zigzag ( $n,0$ ) nanotubes configurations are more likely to form when the diameters are larger 1 nm. The Ti-O covalent bonds were found to be the strongest interactions in TiO<sub>2</sub> tubes, whereas Ti-Ti bonds proved to be much weaker.

One-dimensional (1D) nanostructured materials (nanotubes) have been the focus of extensive research due to their technological importance. Alongside there are the well-known classes of sp<sup>2</sup>-bonded planar structures (graphite, BN, BC<sub>3</sub>, BC<sub>2</sub>N etc) which can be rolled into cylinders (reviews [1, 2, 3, 4, 5, 6]), some efforts are reported also in synthesis and studying of d-metal (M) containing inorganic nanotubes (NT). Nanotubes of layered dichalcogenides MX<sub>2</sub> (M = Mo, W, Ta, Nb etc.; X = S, Se) have been produced [7, 8, 9, 10, 11], and some microscopic models of nanotubular structures formed from layered diborides MB<sub>2</sub> (M = Sc, Ti, Zr) have been proposed recently [12, 13].

On the other hand, much interest was aroused recently in 1D nano-structures (nanowires and nanotubes) based on non-layered semiconducting d-metal oxides such as V<sub>2</sub>O<sub>5</sub> [14, 15, 16, 17, 18, 19], Co<sub>3</sub>O<sub>4</sub> [20, 21], MnO<sub>2</sub> [22], WO<sub>3</sub> [22] etc. Among them 1D nanostructured titania materials have considerable scientific and technological significance due to their chemical inertness, endurance, strong oxidizing power, non-toxicity and lower production cost. Important progress was achieved in synthesis of polycrystalline TiO<sub>2</sub> nanowires and nanotubes using sol-gel template approaches [23, 24, 25, 26, 27, 28].

Recently, the first synthesis of single-crystalline TiO<sub>2</sub> NTs has been performed [29] using unconstrained solution growth method by hydrolyzing TiF<sub>4</sub> under acidic condition without resort to solid templates. Those titania multi-walled nanotubes are constructed with concentric stacking of [101] planes of the anatase polymorph. The diameters (D) of the inner and outer walls are within the range 2,5-5,0 and 20-40 nm, respectively. However, the electronic properties of the titania nanotubes have not been studied up till now.

In this Letter we report the results of our band structure calculations of titania nanotubes constructed from single planes of TiO<sub>2</sub> (anatase). Their electronic properties and bond indices are analyzed as a function of tubes diameters (D) and configuration (*armchair*- and *zigzag*-like).

The anatase structure (space group *I41/amd*) is build up by TiO<sub>6</sub> units. The lattice constants of TiO<sub>2</sub> equal to  $a = 0,3782$ ,  $c = 0,9502$  nm and the internal parameter  $u = d_a/c$ , where  $d_a$  is the apical Ti-O bond length (0,1979 nm) [30].

The structure of the [101] layer (nominal stoichiometry TiO<sub>2</sub>) is shown in Fig. 1. Similar to graphene sheets [1, 2, 3, 4, 5, 6, 7]), sandwich layers (S-M-S) [8, 9, 10, 11, 31, 32]) or metal-boron bilayers [12, 13]) in carbon, MS<sub>2</sub> or MB<sub>2</sub>-based NTs, respectively, these layers can be mapped onto the surface of a cylinder forming "triple-wall" (O-Ti-O) tubes, Fig. 2. As in single-walled carbon NTs [2, 3, 4, 5]), depending on the rolling direction  $\mathbf{c}$  in the 2D lattice  $\mathbf{c} = n\mathbf{a}_1 + m\mathbf{a}_2$  ( $\mathbf{a}_1$ ,  $\mathbf{a}_2$  are primitive vectors for the honeycomb lattice), three groups of TiO<sub>2</sub> 1D-structures can be constructed: *armchair*( $n,n$ )-, *zigzag* ( $n,0$ )-like and *chiral* ( $n,m$ ) nanotubes.

Our calculations were performed for ( $n,0$ ) and ( $n,n$ ) titania NTs as a function  $n$  in ranges from (8,0) to (15,0) and from (4,4) to (15,15), which correspond to the intervals of the inner diameters ( $D^{in}$ ) 0,40 - 1,08 and 0,28 - 2,06 nm, respectively, see Table 1. The largest diameters of our model tubes are comparable with the smallest experimentally observed TiO<sub>2</sub> tubes diameters [29].

The tight binding band structure method within extended Huckel theory (EHT) approximation [33] was employed. Besides the electronic band structure, this approach allows to investigate the chemical bonding based on the Mulliken analysis scheme. The total densities of states (DOS), crystal orbital overlap populations (COOP), and total band energies of the nanotubes ( $E_{tot}$ ) were obtained. The calculated DOS of some ( $n,n$ ) and ( $n,0$ )-like TiO<sub>2</sub> NTs (Fig. 3) are similar for all titania tubes and also agree with DOS of the crystalline anatase [34]. The valence band is composed of two electronic bands separated by a forbidden gap. The lowermost quasi-core band located  $\sim 17$ -16 eV below the

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Fermi level (not shown in Fig. 3) consists mainly of O2s states. The near-Fermi Ti3d-O2p-band is fully occupied, and the lower part of the conduction band is made up predominantly of Ti3d states. The lower energy part of the hybrid band is formed by mixed Ti3d-O2p( $\sigma$ )-states, whereas the upper edge - by non-bonding O2p( $\pi$ ) states. Their distribution depends on the tubes' geometry and diameter and determines the variation in the band gap (BG) width. For the considered NTs with the maximal diameter (minimal curvature), the BG values are  $\sim 3.34$  (*armchair*-like (15,15)NT,  $D^{in} = 2.06$  nm) and  $\sim 3.01$  eV (*zigzag*-like (15,0)NT,  $D^{in} = 1.08$  nm) as compared with the calculated [34] value of  $\sim 2.0$  eV (direct transition at  $\Gamma$ ) and experimentally determined [35] band gap width of crystalline anatase ( $\sim 3.4$  eV). The BG decreases with diminishing NT diameters (Fig. 4a), and for *armchair*-like NTs it being still higher than those for *zigzag*-like NTs. It is of interest that a similar dependence in BG as a function of the tube diameter and configuration was reported for semiconducting NTs based on layered MoS<sub>2</sub> and WS<sub>2</sub> [31, 32].

Figure 4b shows the calculated values of  $E_{tot}$  (per TiO<sub>2</sub> unit) versus titania NT diameters. The  $E_{tot}$  dependence follows  $a\sim 1/D^2$  behavior indicative of a decrease in TiO<sub>2</sub> tubes stability with decreasing D. Analogous dependencies of strain energy (the difference between the energies of the plane atomic layer and the corresponding NT characterizes the chemical stability of tubular structures) are known for carbon and the majority of non-carbon tubes [1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 31, 32]. It is worth noting that our results show that for small diameters ( $D^{in} < 1$  nm) *armchair*-like configurations are more stable, whereas for large diameters *zigzag*-like configurations of titania NTs have greater stability, Fig. 4b.

The formation of the covalent bonds in a tube can be readily seen from the COOP values (Table 1). For all tubes, (I) the main bonds are Ti-O interactions; (II) the occupation of the Ti-Ti bonds is by an order of magnitude smaller; (III) O-O bonding are absent (COOPs  $< 0$ ); and (IV) there is a sharp anisotropy of separate Ti-O bonds depending both on their orientation relative to the TiO<sub>2</sub> tube axis and between the bonds of titanium and oxygen atoms belonging to inner ( $O^{in}$ ) or outer ( $O^{out}$ ) oxygen cylinders. For *zigzag*-like tubes, the main bonds are Ti- $O^{out}$ . As D increases, their anisotropy decreases. For *armchair*-like tubes, the COOPs values of Ti- $O^{in}$  and Ti- $O^{out}$  are comparable.

It should be noted that the total energy versus diameter dependence is almost saturated at  $D > 1.2$  nm and the asymptotic value of  $E_{tot}$  is slightly depends from diameter up to 2.4 nm. The weak dependence of BG from diameter for large values of D is also observed (Fig 4a).

In summary, single-walled titania nanotubes with nominal stoichiometry TiO<sub>2</sub> were modeled and their electronic properties and bonding indices have been investigated using the tight-binding band theory. We show that both *zigzag*- and *armchair*-like nanotubes are semiconducting, and the band gap trends to vanish for very small NT diameters. *Zigzag* titania nanotubes were found to form more readily for diameters comparable with those observed experimentally [29]. It was established that Ti-O covalent bonds are the strongest in TiO<sub>2</sub> tubes, whereas Ti-Ti bonds are much weaker.

There are numerous issues of interest for future studies. First of all, an important problem is the effect of "interlayer" interactions on the properties of multi-walled TiO<sub>2</sub> tubes, as well as simulation of the types of polyhedra, which close the open ends of the tubes. A probable factor of titania NT electronic properties variation is "polygonization" of their walls (flattened segments of [101] planes in the tube walls were observed experimentally [29]), which calls for investigations of radially deformed tubes.

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- [1] M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San-Diego, 1996).
  - [2] R. Saito, G. Dresselhaus, M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
  - [3] P. Moriarty, Rep. Progr. Phys. **64**, 297 (2001).
  - [4] R. Knupfer, Surf. Sci. Rep. **42**, 1 (2001).
  - [5] P.M. Ajayan, O.Z. Zhou, Carbon Nanotubes **80**, 391 (2001).
  - [6] A.L. Ivanovskii, Russ. Chem. Rev. **71**, 203 (2002).
  - [7] A. Rothschild, J. Sloan, R. Tenne, J. Am. Chem. Soc. **122**, 5169 (2000).
  - [8] R. Tenne, Prog. Inorg. Chem. **50**, 269 (2001).
  - [9] M. Nath, C.N.R. Rao, J. Am. Chem. Soc. **123**, 4841 (2001).
  - [10] R. Rosentsveig, A. Margolin, Y. Feldman, R. Popovitz-Biro, R. Tenne, Appl. Phys. **A74**, 367 (2002).
  - [11] R. Tenne, Colloids Surf. **A208**, 83 (2002).
  - [12] L.A. Chernozatonskii, JEPT Letters **74**, 467 (2001).
  - [13] V.V. Ivanovskaya, A.N. Enyashin, A.A. Sofronov, Yu.N. Makurin, N.I. Medvedeva, A.L. Ivanovskii, J. Mol. Struct.: THEOCHEM (**in press**) (2002).
  - [14] F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, B. Schnyder, R. Nesper, J. Amer. Chem. Soc. **121**, 8324 (1999).
  - [15] F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, R. Nesper, Z. Anorgan. Allg. Chem. **626**, 2208 (2000).
  - [16] E. Muller, F. Krumeich, Ultramicroscopy **84**, 143 (2000).

- [17] H.-J. Muhr, F. Krumeich, U.P. Schonholzer, F. Bieri, M. Niederberger, L.J. Gauckler, R. Nesper Adv. Mater., **12**, 231 (2000).
- [18] M. Niederberger, H.-J. Muhr, F. Krumeich, F. Bieri, D. Gunter, R. Nesper, Chem. Mater. **12**, 1995 (2000).
- [19] K.S. Pillai, F. Krumeich, H.-J. Muhr, M. Niederberger, R. Nesper, Solid State Ionics **185**, 141 (2001).
- [20] X. Shi, S. Han, R.J. Sanedrin, C. Galvez, D.G. Ho, B. Hernandez, F. Zhou, M. Selke, Nano Lett. **2**, 289 (2002).
- [21] X. Shi, S. Han, R.J. Sanedrin, F. Zhou, M. Selke, Chem. Mater. **14**, 1897 (2002).
- [22] B.B. Lakshmi, C.J. Patrissi, C.R. Martin, Chem. Mater. **9**, 2544 (1997).
- [23] H. Imai, Y. Takei, K. Shimizu, M. Matsuda, H.J. Hirashima, Mater. Chem. **9**, 2971 (1999).
- [24] K. Shimizu, H. Imai, H. Hirashima, K. Tsukuma, Thin Solid Films **351**, 220 (1999).
- [25] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Adv. Mater. **11**, 1307 (1999).
- [26] H. Imai, M. Matsuda, K. Shimitzu, H. Hirashima, N. Negishi, J. Mater. Chem. **10**, 2005 (2000).
- [27] D.S. Seo, J.K. Lee, H. Kim, J. Crystal Growth **229**, 428 (2001).
- [28] Z. Miao, D. Xu, J. Ouyang, G. Guo, X. Zhao, Y. Tang, Nano Lett. **2**, 717 (2002).
- [29] S.M. Liu, L.M. Gan, L.H. Liu, W.D. Zhang, H.C. Zeng, Chem. Mater. **14**, 1391 (2002).
- [30] J.K. Burdett, G.J. Hughbanks, G.J. Miller, J.W. Richardson, J.V. Smith, J. Am. Chem. Soc. **109**, 3639 (1987).
- [31] G. Seifert, H. Terrones, M. Terrones, G. Jungnickel, Th. Frauenheim, Solid State Commun. **114**, 245 (2000).
- [32] G. Seifert, H. Terrones, M. Terrones, G. Jungnickel, Th. Frauenheim, Phys. Rev. Lett. **85**, 146 (2000).
- [33] R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures* (VCH, New York, 1988).
- [34] R. Asahi, Y. Taga, A.J. Freeman, Phys. Rev. **B61**, 7459 (2000).
- [35] Y. Tang, H. Berger, P.E. Schmidt, F. Levy, G. Burri, Solid State Commun. **23**, 161 (1977).

TABLE I: The number of atoms in unit cells, diameters (D, nm) and indices of intra-atomic bonds (COOPs, e) for TiO<sub>2</sub> nanotubes.

Tubes	Cell size	$D^{in}$	$D^{out}$	COOPs**					
				Ti-O <sup>in</sup> <sub>1</sub>	Ti-O <sup>in</sup> <sub>2</sub>	Ti-O <sup>out</sup> <sub>1</sub>	Ti-O <sup>out</sup> <sub>2</sub>	Ti-Ti <sub>1</sub>	Ti-Ti <sub>2</sub>
(8,0)	48	0,422	0,896	0	0	0,499	0,331	0,041	0,028
(9,0)	54	0,518	0,992	0	0	0,488	0,349	0,021	0,005
(10,0)	60	0,614	1,082	0	0	0,477	0,351	0,018	0,001
(11,0)	66	0,708	1,174	0	0	0,470	0,353	0,018	0
(12,0)	72	0,800	1,266	0	0	0,464	0,354	0,017	0
(13,0)	78	0,894	1,356	0	0	0,458	0,355	0,017	0
(14,0)	84	0,986	1,448	0	0	0,453	0,355	0,017	0
(15,0)	90	1,076	1,538	0	0	0,449	0,356	0,017	0
(4,4)	24	0,286	0,782	0,117	0,302	0,241	0,302	0,004	0,036
(5,5)	30	0,464	0,946	0,181	0,279	0,235	0,308	0	0,031
(6,6)	36	0,632	1,108	0,218	0,285	0,229	0,310	0	0,029
(7,7)	42	0,798	1,268	0,242	0,292	0,224	0,312	0	0,029
(8,8)	48	0,960	1,426	0,258	0,298	0,219	0,313	0	0,029
(9,9)	54	1,120	1,584	0,270	0,302	0,216	0,314	0	0,029
(10,10)	60	1,278	1,742	0,279	0,305	0,213	0,315	0	0,030
(11,11)	66	1,436	1,900	0,287	0,307	0,210	0,315	0	0,030
(12,12)	72	1,594	2,056	0,293	0,309	0,208	0,316	0	0,030
(13,13)	78	1,750	2,212	0,298	0,310	0,206	0,316	0	0,030
(14,14)	84	1,906	2,368	0,303	0,311	0,204	0,316	0	0,030
(15,15)	90	2,064	2,524	0,306	0,312	0,202	0,316	0	0,030

\*  $D^{in}$ ,  $D^{out}$  - diameters of "inner" and "outer" cylinders made up of oxygen atoms.

\*\* Indices 1, 2 correspond to paired bonds with a different orientation along the tube axis (see Fig. 1); Ti-O<sup>in</sup> and Ti-O<sup>out</sup> are the bonds of Ti with atoms of the "inner" and "outer" oxygen cylinders.

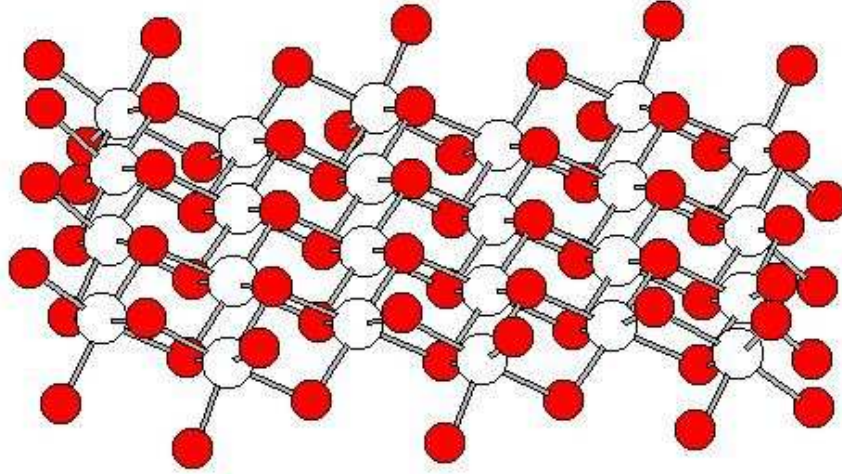


FIG. 1: Top view on the structure of [101] layer TiO<sub>2</sub> (anatase).

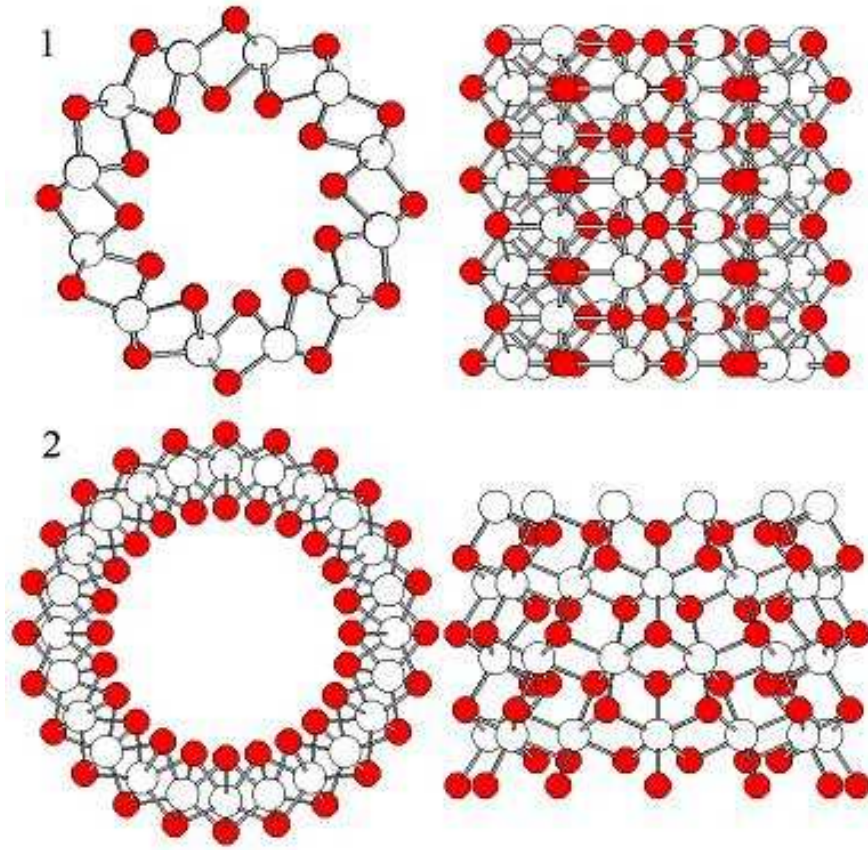


FIG. 2: The structure of 1-armchair (6,6) and 2-zigzag (12,0) TiO<sub>2</sub> NTs. Side views and views along the tube axis are shown.

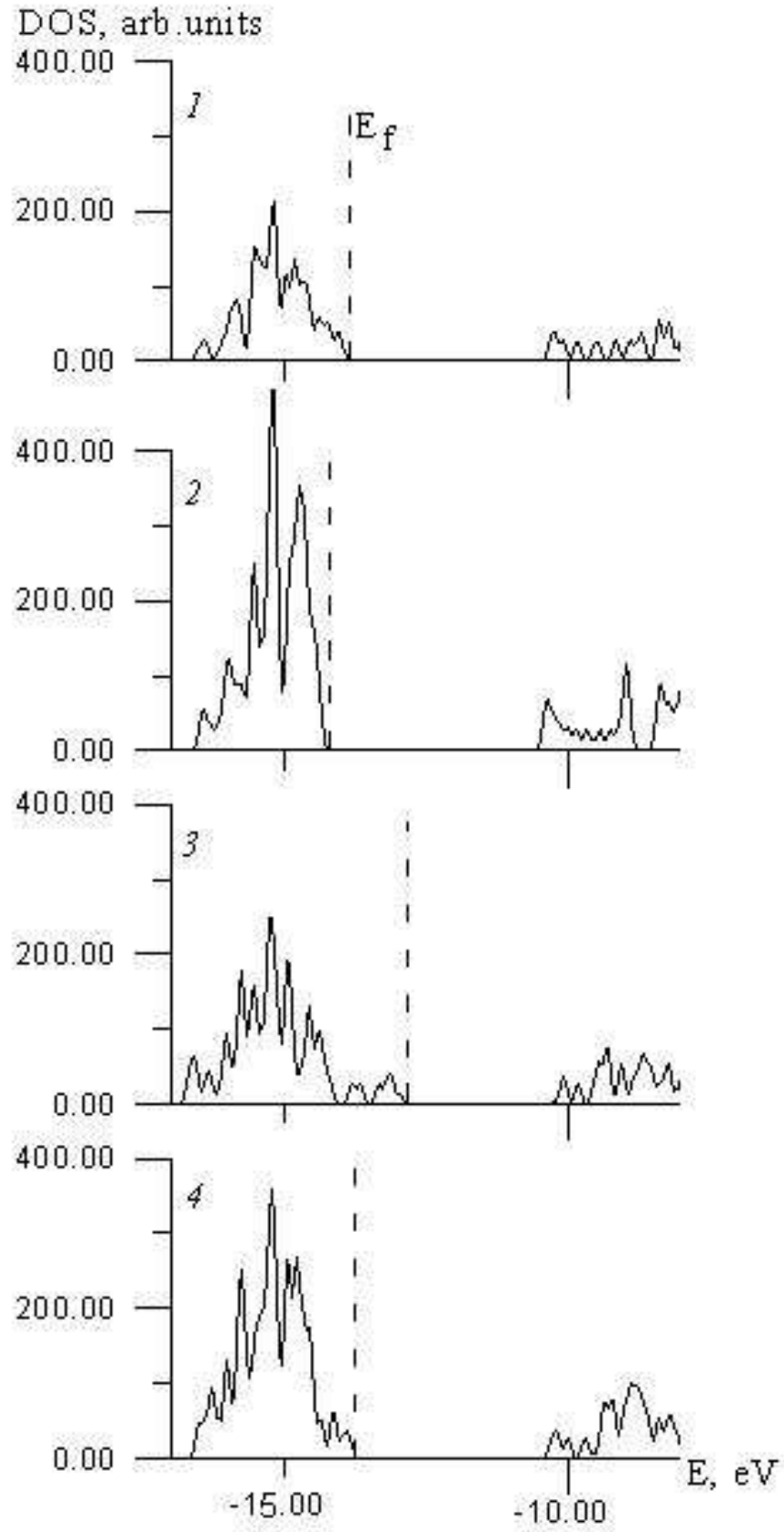


FIG. 3: Total DOS of *armchair* (8,8), (15,15) (1,2) and *zigzag* (11,0), (15,0) (3,4) TiO<sub>2</sub> nanotubes.

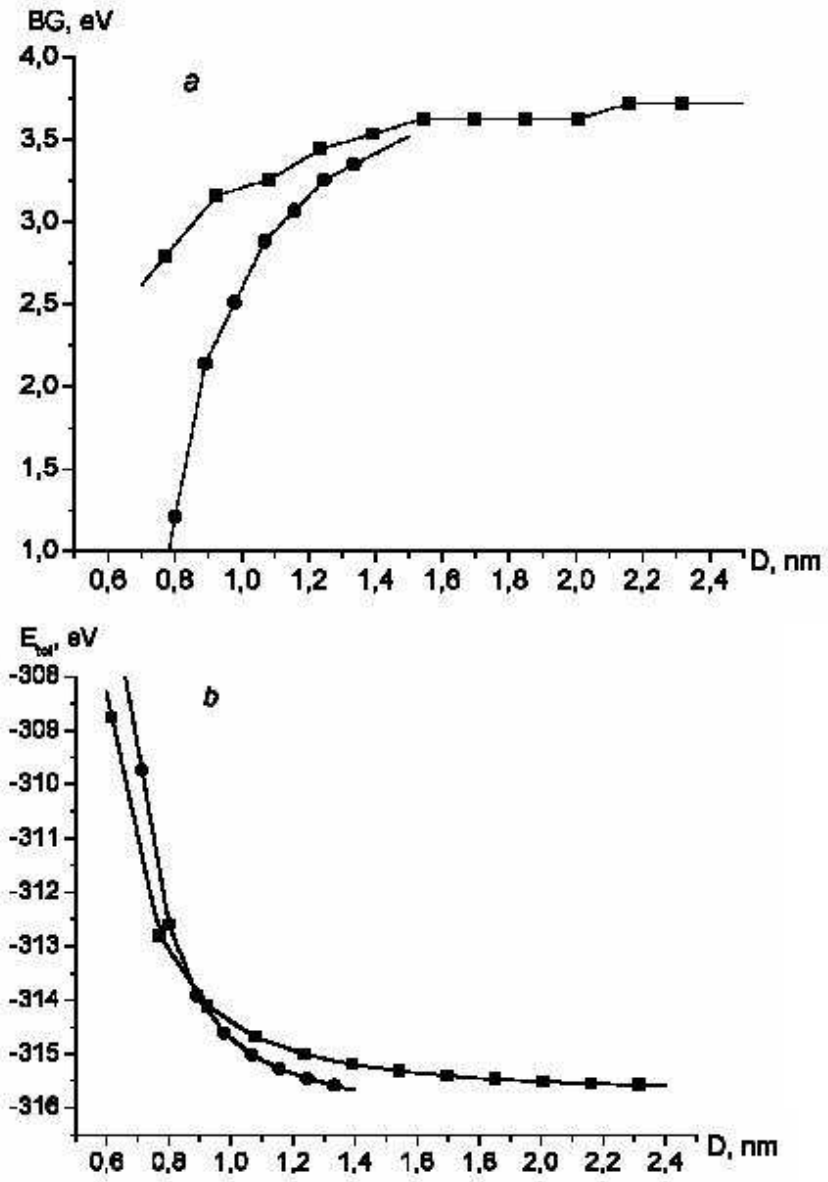


FIG. 4: Band gap (a) and total energies (per  $\text{TiO}_2$  unit)(b) of *armchair* (it  $n,n$ ) - squares and *zigzag* ( $n,0$ ) - circles as a function of the diameter of Ti cylinder.